



Europäisches Patentamt
European Patent Office
Office européen des brevets



⑪ Publication number: 0 666 304 A1

⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: 94870020.8

㉓ Int. Cl. 6: C11D 3/20, C11D 1/62,
C11D 1/90, C11D 1/92,
C11D 1/94, C23G 1/02,
C23G 1/08, C02F 5/10,
C02F 5/12

㉒ Date of filing: 03.02.94

㉔ Date of publication of application:
09.08.95 Bulletin 95/32

㉕ Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU NL
PT SE

㉖ Applicant: THE PROCTER & GAMBLE
COMPANY
One Procter & Gamble Plaza
Cincinnati,
Ohio 45202 (US)

㉗ Inventor: Carrié, Michel Jean
Av. de Limburg Stirum 235
B-1780 Wemmel (BE)
Inventor: Vos, Eddy
Koetsiersweg 15
B-3210 Linden (BE)

㉘ Representative: Engisch, Gautier et al
Procter & Gamble
European Technical Center N.V.
Temselaan 100
B-1853 Strombeek-Bever (BE)

㉙ Acidic cleaning compositions.

㉚ Aqueous compositions comprise maleic acid and a surfactant consisting of a cationic surfactant, a zwitterionic surfactant, an amphoteric surfactant or mixtures thereof. Said compositions are substantially odor-free and do not contain any perfume.

EP 0 666 304 A1

Technical field

The present invention relates to cleaning compositions for hard-surfaces. More specifically, compositions are described which comprise surfactants which are substantially odor-free. Indeed, said compositions give optimal performance in removing limescale stains and encrustations while being odor-free and are particularly adapted for descaling appliances.

Background

10 It is well known in the art that limescale deposits can be chemically removed with acidic solutions, and a great variety of acidic cleaning compositions have been described for this purpose.

Furthermore, it is known in the art to use surfactants in such acidic compositions to lower the surface tension and to improve the wettability of the surfaces being cleaned. The presence of surfactants in such compositions helps to solubilize the soils and to improve the streaking profile of the acids, thereby also 15 slowing down the limescale redeposition phenomenon.

20 However, the presence of surfactants causes the problem that a base odor is imparted to the compositions comprising them, thereby making them not attractive from a consumer point of view. This base odor, chemical in nature, can be due to the surfactant molecules themselves, to the presence of unreacted intermediates from the surfactant making process or to other impurities within the surfactant raw materials.

25 To overcome this problem it is well known in the art to add a perfume in surfactant-based compositions, one of its role being to effectively mask the surfactants base odor. However, it has been found that perfumes tend to deposit onto synthetic materials and are thus difficult to rinse off.

30 This is even more of a problem in applications such as the descaling of appliances including cooking appliances (e.g. coffee machine), beauty care appliances (e.g. dental jet machine) or any other appliance such as steam irons, kettles and the like, as said appliances comprise various synthetic surfaces. Indeed, during the descaling operation of such an appliance perfumes firstly tend to deposit onto the synthetic surfaces and then tend to be released during the normal use of said appliance. In other words, food or beverage can be contaminated during the normal use of a cooking appliance, when said normal use follows 35 the descaling operation of said appliance with a composition comprising perfumes. This is highly undesirable from a consumer acceptance viewpoint. Thus it is desirable to use descaling compositions being free of perfumes.

35 It is therefore an object of the present invention to provide a composition comprising surfactants and an organic acid, for the removal of limescale deposits, said composition being free of perfume and possessing a superior limescale removing capacity while being also substantially odor-free.

40 It has now been found that compositions comprising an organic acid being substantially odor-free such as maleic acid together with a surfactant consisting of cationic, zwitterionic, amphoteric surfactants or mixtures thereof are substantially odor-free without the need of adding any further compound such as a perfume to mask the surfactants base odor. Indeed, we have found that cationic, zwitterionic, amphoteric surfactants or mixtures thereof do not impart a base odor to a composition, or to the surfaces treated with 45 said composition, provided that the pH of the composition is neutral or maintained in the acidic range. Unexpectedly the compositions of the present invention comprising maleic acid and such a surfactant or mixtures thereof under neutral or acidic conditions, are substantially odor-free compared to the same compositions with equivalent amount of other surfactant types such as anionic, nonionic, amine oxide surfactants or mixtures thereof.

45 An advantage of the present invention is that said compositions are particularly suitable for applications in which the presence of perfume is not desirable including the descaling of appliances such as cooking appliances, beauty care appliances or any other appliance such as steam irons, kettles, coffee machines, tea pots and the like.

50 A further advantage is that the compositions of the present invention are also safe to a wide variety of materials used to manufacture said appliances, including synthetic materials as well as any type of metal (e.g. aluminum, stainless steel, chromed steel and the like).

55 European patent application No. 93870120.8 discloses an acidic composition comprising an acid for example maleic acid together with a thickening system comprising from 0.5% to 15% by weight of the total composition of a mixture of a nonionic surfactant and a cationic surfactant. No reference is made to the possibility to provide substantially odor-free surfactants based compositions due to the use of said cationic surfactants as the surfactant.

GB 2071 688 and EP 255 978 disclose acidic compositions comprising among other ingredients from 0.1% to 10% by weight of cationic surfactants and a strong inorganic acid. Organic acids and in particular maleic acid are not disclosed. No reference is made to the possibility to provide substantially odor-free surfactants based compositions due to the use of said cationic surfactants as the surfactant.

5

Summary of the invention

The present invention is an aqueous composition having a pH of from 0.1 to 7 comprising an organic acid, a surfactant and is free of any perfume. Said surfactant consists of a cationic, zwitterionic or 10 amphoteric surfactant or mixtures thereof.

The present invention also encompasses a process of descaling appliances wherein an acidic composition comprising a cationic surfactant, a zwitterionic surfactant, an amphoteric surfactant or mixtures thereof, is applied in its neat form or in its diluted form to said appliances, then left to act and then removed by rinsing.

15

Detailed description of the invention

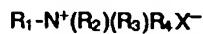
The compositions according to the present invention are designed for removing limescale deposits. Thus they comprise as a first essential ingredient an organic acid such as maleic acid. Said organic acid is 20 also per se substantially odor-free. The compositions according to the present invention comprise from 0.1% to 45% by weight of the total composition of maleic acid, preferably from 1% to 25% and more preferably from 8% to 20%. This percentage is calculated on the basis of the molecular weight of the acid form, but maleic anhydride is equally convenient for use in the compositions according to the present invention. Indeed maleic anhydride is generally cheaper and it is transformed into the acid form when 25 incorporated in an aqueous medium. In a preferred embodiment of the present invention maleic acid is used alone. However, other acids which are particularly efficient in removing limescale deposits may be used in addition to said organic acid, at levels at which they do not impart a base odor to the compositions. Such optional acids are for example sulfonic acids such as sulfamic acid or methanesulfonic acid, 30 hydrochloric acid, citric acid, phosphoric acid or mixtures thereof. In another embodiment of the present invention maleic acid is used together with sulfonic acids such as sulfamic acid or methanesulfonic acid or/and citric acid.

The compositions according to the present invention comprise as a second essential ingredient a surfactant consisting of a cationic, a zwitterionic or an amphoteric surfactant or mixtures thereof. The compositions according to the present invention comprise from 0.01% to 10% of said surfactant, preferably 35 from 0.01% to 5%, more preferably from 0.01% to 2%. In a preferred embodiment of the present invention where the compositions are used to descale appliances the surfactant is present at a level below 1% by weight of the total composition, preferably from 0.01% to 0.9% and more preferably from 0.05% to 0.8%. It is possible to use mixtures of a type of surfactant or of different types of surfactants hereinafter described, without departing from the spirit of the present invention.

40 It is preferred to use cationic surfactants in the compositions of the present invention. Suitable cationic surfactants to be used herein include derivatives of quaternary ammonium, phosphonium, imidazolium and sulfonium compounds. Preferred cationic surfactants for use herein are according to the formula $R_1 R_2 R_3 R_4 N^+ X^-$, wherein X is a counteranion, R_1 is a C_8 - C_{20} hydrocarbon chain and R_2 , R_3 and R_4 are independently selected from H or C_1 - C_4 hydrocarbon chains. In a preferred embodiment of the present invention, R_1 is a C_{12} - C_{18} hydrocarbon chain, most preferably C_{14} , C_{16} or C_{18} , and R_2 , R_3 and R_4 are all three methyl, and X is halogen, preferably bromide or chloride, most preferably bromide. Examples of cationic surfactants are stearyl trimethyl ammonium bromide (STAB), cetyl trimethyl ammonium bromide (CTAB) and myristyl trimethyl ammonium bromide (MTAB).

50 Suitable zwitterionic surfactants to be used herein contain both cationic and anionic hydrophilic groups on the same molecule at a relatively wide range of pH's. The typical cationic group is a quaternary ammonium group, although other positively charged groups like phosphonium, imidazolium and sulfonium groups can be used. The typical anionic hydrophilic groups are carboxylates and sulfonates, although other groups like sulfates, phosphonates, and the like can be used. A generic formula for some preferred zwitterionic surfactants is

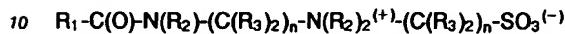
55



wherein R_1 is a hydrophobic group; R_2 and R_3 are each C_1 - C_4 alkyl, hydroxy alkyl or other substituted alkyl

group which can also be joined to form ring structures with the N; R₄ is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 4 carbon atoms; and X is the hydrophilic group which is preferably a carboxylate or sulfonate group. Preferred hydrophobic groups R₁ are alkyl groups containing from 8 to 22, preferably less than 18, more preferably less than 16 carbon atoms. The hydrophobic group can contain unsaturation and/or substituents and/or linking groups such as aryl groups, amido groups, ester groups and the like. In general, the simple alkyl groups are preferred for cost and stability reasons.

Other specific zwitterionic surfactants have the generic formulas:



or



wherein each R₁ is a hydrocarbon, e.g. an alkyl group containing from 8 up to 20, preferably up to 18, more preferably up to 16 carbon atoms, each R₂ is either a hydrogen (when attached to the amido nitrogen), short chain alkyl or substituted alkyl containing from one to 4 carbon atoms, preferably groups selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, 20 preferably methyl, each R₃ is selected from the group consisting of hydrogen and hydroxy groups and each n is a number from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any (C(R₃)₂) moiety. The R₁ groups can be branched and/or unsaturated. The R₂ groups can also be connected to form ring structures. Preferred herein is a surfactant of this type, a C₁₀-C₁₄ fatty acylamidopropylene (hydroxypropylene) sulfobetaine that is available from the Sherex Company under the 25 trade name "Varion CAS sulfobetaine"®.

Suitable amphoteric surfactants to be used herein are surfactants which are similar to the zwitterionic surfactants but without the quaternary group. Indeed, they contain an amine group instead of the quaternary group. They contain said amine group that is protonated at the low pH of the composition to form cationic group and they may also possess an anionic group at these pHs.

30 The third essential feature of the compositions of the present invention is their pH. The compositions according to the present invention have a pH of from 0.1 to 7. Indeed, it has been found that the surfactants as defined in the present invention are substantially odor-free under neutral and acidic conditions whereas the same compounds impart a base odor to a composition comprising them under alkaline conditions. However, the limescale removing capacity of a composition according to the present invention is strongly 35 dependent on its pH, and the lower the pH, the better the limescale removing capacity. Thus, the compositions according to the present invention preferably have a pH as is in the range of from 0.1 to 5, more preferably of from 0.1 to 3 and most preferably of from 0.5 to 2.

It has been observed that compositions according to the present invention having a pH of from 0.1 to 7 comprising an organic acid such as maleic acid together with a surfactant consisting of a cationic, 40 zwitterionic, amphoteric surfactant or mixtures thereof, are substantially odor free compared to similar compositions comprising equivalent amount of other surfactant types such as anionic, nonionic surfactants, amine oxide surfactants or mixtures thereof. Indeed, the use of the cationic, zwitterionic, amphoteric surfactants or mixtures thereof according to the present invention in hard-surfaces limescale removing compositions comprising maleic acid and no perfume improves the base odor of said compositions.

45 By "improving the base odor" it is to be understood that the smell due to the presence of surfactants in a composition having a pH of from 0.1 to 7 is reduced when the surfactant used in said composition is a cationic surfactant, a zwitterionic, an amphoteric surfactant or mixtures thereof as defined in the present invention. A method suitable for measuring "the base odor improvement", i.e. the smell reduction phenomenon, is an olfactory grading method mentioned hereinafter in the examples. In said method 50 professional perfumers give a description of the odor (e.g. amine, fatty) as well as an evaluation of the odor impact (e.g. weak or strong).

Furthermore, it has now been found that acidic compositions comprising maleic acid together with a surfactant consisting of the surfactant hereinbefore described, at a level below 1% by weight of the total 55 composition, are particularly suitable for descaling applications where good wetting and low sudsing properties are essential but in which the presence of a surfactant base odor or the presence of perfumes to mask said odor is not desirable from a consumer acceptance. A typical such application is the descaling of cooking appliances such as coffee machines, of beauty care appliances or even of any appliance where the presence of perfumes and/or any base odor is not desirable (steam irons, kettles, and the like).

The compositions according to the present invention are aqueous. Accordingly, the compositions according to the present invention comprise from 10% to 95% by weight of the total composition of water, preferably from 50% to 90%, most preferably from 70% to 85%.

5 The compositions according to the present invention may further comprise a variety of other ingredients including colorants, bactericide, thickeners, dyes, chelants, pigments, solvents, stabilizers, corrosion inhibitors and the like.

10 The present invention also encompasses a process of descaling appliances wherein an acidic composition comprising a surfactant consisting of a cationic, a zwitterionic, an amphoteric surfactant or mixtures thereof is applied in its neat form or in its diluted form to said appliances, then left to act and then removed by rinsing.

15 The expression "applied in diluted form" herein includes dilution by the user, which occurs for instance in the application of descaling appliances. Typical dilution levels are of from 0.5% to 50% of the compositions.

20 The compositions herein are also particularly suitable to be used in hot conditions, e.g. when descaling a coffee machine said compositions can be used neat or diluted and in hot conditions (80 °C to 180 °C).

25 The present invention is further illustrated by the following experimental data and examples.

Experimental data

20 1)

Compositions according to the present invention were evaluated in terms of their base odor with an olfactory grading test method.

25 For this purpose compositions according to the present invention have been prepared. These compositions are made comprising the listed ingredients in the listed proportions (weight %).

30	Ingredients: (% by weight)	Compositions			
		1	2	3	4
35	Maleic acid	6	6	6	14
	MTAB*	3	/	/	/
	Cocoamido propyl hydroxysulfobetaine**	/	3	/	/
	Amine oxide	/	/	3	/
	Lutensol AO 7***	/	/	/	0.5
40	Waters & Minors	—up to 100—			

* MTAB is myristic trimethylammonium bromide (cationic surfactant).

** Cocoamido propyl hydroxysulfobetaine is a zwitterionic surfactant.

*** Lutensol AO7 is a nonionic surfactant.

40

45 The odor evaluation was conducted by a panel of two professional perfumers who evaluated compositions 1, 2, 3 and 4 at three different pH values (e.g. highly acidic, neutral and highly basic) placed in blind bottles. Each panelist smelled each of the three pH variations of the above compositions and gave a description of the odor per se in terms of fatty, amine, waxy or aldehyde odor as well as an evaluation of the odor impact itself.

Odor test results:

50

Comp.	1	2	3	4
pH = 1.5	neutral	weak fatty	green waxy strong fatty	fatty
pH = 7	neutral	weak fatty	waxy strong fatty	/
pH = 12	strong amine	strong fatty	aldehyde weak fatty	/

55 The results show that composition 1 based on a cationic surfactant has a strong amine odor under alkaline conditions whereas under neutral and acidic conditions said composition 1 smells neutral, i.e. is

substantially odor-free. The results also show that composition 2 based on a zwitterionic surfactant has a strong fatty odor under alkaline conditions whereas under neutral and acidic conditions said composition 2 has an improved base odor (weak fatty odor). Furthermore, in contrast to compositions 1 and 2 which show an improved base odor under neutral and acidic pH conditions, composition 3 which includes amine oxide 5 as a surfactant does not display a better base odor in acid medium compared to alkaline conditions. The results also show that composition 4 which includes a nonionic surfactant does smell (fatty odor) under acidic conditions (pH=1.5) compared to compositions 1 and 2 which are substantially odor free at the same pH.

Thus, according to the present invention compositions comprising maleic acid and as a surfactant a 10 cationic surfactant or a zwitterionic surfactant are substantially base odor free under neutral and acidic conditions compared to the same compositions having other surfactant types as for example amine oxide or nonionic surfactants.

2)

15

Further examples of compositions according to the present invention are the following. These compositions are made comprising the listed ingredients in the listed proportions (weight %).

	Ingredients: (% by weight)	Compositions		
		1	2	3
	Maleic acid	19	16	14
	Citric acid	/	3	3
	Sulfamic acid	/	/	2
	MTAB*	0.2	0.2	0.2
	Waters & Minors	up to 100		

MTAB* is myristic trimethylammonium bromide (cationic surfactant).

30

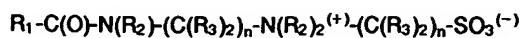
All the compositions according to the examples above exhibit superior limescale performance while being substantially odor free.

Claims

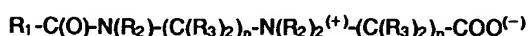
35

1. An aqueous composition having a pH of from 0.1 to 7 comprising an organic acid and a surfactant, characterized in that said surfactant consists of cationic, zwitterionic, amphoteric surfactants or mixtures thereof and in that said composition is perfume-free.
2. A composition according to claim 1 wherein said composition is a limescale removing composition having a pH of from 0.1 to 5, preferably of from 0.1 to 3 and more preferably of from 0.5 to 2.
3. A composition according to claim any of the preceding claims wherein said organic acid is maleic acid.
4. A composition according to claim 3 comprising from 0.1% to 45% by weight of the total compositions of said acid, preferably from 1% to 25% and more preferably from 8% to 20%.
5. A composition according to any of the preceding claims comprising from 0.01% to 10% by weight of the total compositions of said surfactant, preferably from 0.01% to 5% and more preferably from 0.01% to 2%.
6. A composition according to any of the preceding claims wherein said surfactant is a cationic surfactant of the formula $R_1 R_2 R_3 R_4 N^+ X^-$, wherein X is a counteranion, R_1 is a C_8 - C_{20} hydrocarbon chain and R_2 , R_3 and R_4 are independently selected from H or C_1 - C_4 hydrocarbon chains or mixtures thereof.
7. A composition according to claim 6 wherein in said cationic surfactant X is bromide or chloride, R_1 is a C_{12} - C_{18} hydrocarbon chain, most preferably C_{14} , C_{16} or C_{18} and R_2 , R_3 and R_4 are all three methyl.

8. A composition according to claims 1 to 5 wherein said surfactant is a zwitterionic surfactant of the formula



or



15 wherein each R_1 is an alkyl group containing from 8 up to 20, preferably up to 18, more preferably up to 16 carbon atoms, each R_2 is either a hydrogen, when attached to the amido nitrogen, short chain alkyl or substituted alkyl containing from 1 to 4 carbon atoms, preferably groups selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, preferably methyl, each R_3 is selected from the group consisting of hydrogen and hydroxy groups and each n is a number from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any $(C(R_3)_2)$ moiety or mixtures thereof.

20 9. A composition according to claim 8 wherein said zwitterionic surfactant is a $C_{10}-C_{14}$ fatty acylamidopropylene(hydroxypropylene)sulfobetaine.

25 10. A composition according to any of the preceding claims wherein said composition further comprises sulfamic acid, methanesulfonic acid, citric acid, phosphoric acid, hydrochloric acid or mixtures thereof.

30 11. A process of descaling appliances wherein an acidic composition comprising a surfactant consisting of cationic, zwitterionic, amphoteric surfactants or mixtures thereof is applied in its neat form or in its diluted form to said appliances, then left to act and then removed by rinsing.

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 87 0020

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 411 708 (COLGATE - PALMOLIVE CO.) * page 3, line 1 - line 2; claims 1,7-9,12-16 *	1-3,10	C11D3/20 C11D1/62 C11D1/90 C11D1/92 C11D1/94 C23G1/02 C23G1/08 C02F5/10 C02F5/12
X	US-A-5 061 393 (LINARES ET AL.) * column 6, line 65 - column 7, line 6; claims 1-3,14 *	1,8 10	C23G1/02 C23G1/08
X	EP-A-0 228 501 (J.A.BENCKISER GMBH.) * page 6 * * page 9, paragraph 3 -paragraph 4 * * claims 1,2,5,6 *	1,8,10	C02F5/10 C02F5/12
X	EP-A-0 336 878 (COLGATE - PALMOLIVE CO.) * column 2, line 28 - line 49; claim 1 *	1	
X	GB-A-2 106 927 (COLGATE - PALMOLIVE CO.) * page 1, line 74 - page 2, line 39 * * claim 1 *	1	
D,E	EP-A-0 601 990 (THE PROCTER & GAMBLE CO.) * claims *	1-7	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D C23G C02F
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	22 June 1994	Serbetsoglou, A.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- M : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			